Paper Technology Plan

September 26, 1991

I. Introduction

The paper technology program has as its overall objective the development of proprietary cigarette papers for new products. The specific applications at this time are: 1) products with reduced sidestream visibility; 2) papers which will control puff count and reduce ash flaking on ultra low delivery cigarettes; 3) papers which will allow control of burn rate for Project Tomorrow; 4) development of filter materials which can be used to make filters with surface areas equivalent to paper filters, but with surface adsorption characteristics similar to cellulose acetate; 5) the determination of specifications for cigarette papers which will be consistent with current cigarette specifications; 6) improved tipping papers; and 7) products for aroma modification of sidestream. Each of these applications will be covered in detail below.

II. Products with Reduced Sidestream Visibility

A. Objectives

1. To develop a proprietary cigarette wrapper which will reduce visible sidestream smoke by at least 70% in a full circumference cigarette, as compared to an appropriate control, with subjectives equivalent to a conventional cigarette by 1992.

2. To develop proprietary cigarette wrappers which will, in addition to reducing sidestream visibility, reduce sidestream odor and irritation by 1995.

The second objective was added in 1990. Little work is planned to take place addressing this objective in 1991. It is anticipated, however, that by the end of 1991 several different systems which provide reduced visibility will be available for product development work. Resources will then be phased into research on technology to give products with reduced odor and irritation.

B. Introduction and Status

Philip Morris has been working on cigarettes with reduced sidestream visibility for about ten years. Work was initiated with the commercial introduction of a reduced sidestream brand, Passport, in Canada, and has grown in importance during the intervening years as a consequence of the public's growing, although misplaced, concern over passive smoke. Passport utilized a paper manufactured by Ecusta containing 12% magnesium hydroxide. The product had serious subjective problems and was not a commercial success. During the first seven years that R&D was involved in a reduced sidestream program we depended on our two suppliers, Ecusta and Kimberly-Clark, to provide us with low sidestream papers. Three years ago, however, a decision was made to attempt to develop our own low sidestream paper. This was done first of all because our suppliers have not been strikingly successful in providing us with a paper which will achieve our objectives. More importantly, however, it is essential that we develop our own proprietary papers to obtain a clear competitive advantage. In 1989 we developed a slim cigarette with sidestream reduction which met our target and acceptable subjectives. This product utilizes a double wrap system. The outer wrap was developed jointly by PM and Kimberly-Clark. It has a 45 g/m^2 basis weight, contains 35% calcium carbonate with a surface area of 20 m^2/g, and contains potassium succinate, monoammonium phosphate (MAP) and sodium carboxymethyl cellulose (CMC) as additives. The inner wrap is a thin (18 g/m^2) paper with 3% low surface area calcium carbonate and 2% potassium citrate. This product was introduced nationally in September, 1989. Neither the system used on the slim cigarette nor the Ecusta magnesium hydroxide paper, however, has proved to be satisfactory for a full circumference cigarette. Both wrappers give products with significant subjective problems.

Significant success was achieved in 1990 with the development of a single wrap, calcium carbonate containing wrapper for a full circumference cigarette. This wrapper had a basis weight of 45 g/m^2 , contained 33% Multifex calcium carbonate, and used about 13% mono potassium phosphate as a fluxing agent and had a porosity of 6 Coresta. Charcoal-filtered cigarettes made with this paper gave about 55-60% sidestream visibility reduction, and did reasonably well with respect to liking scores on a POL versus Benson & Hedges Lights. A variation of this paper has also been developed as a single wrap for Superslims to take the place of the current double wrap. There is little more work planned in 1991 with this type of paper; except assist in refining cigarette design acceptability. Most of the effort in this area will be devoted to the synthesis and evaluation of various types of magnesium carbonates as inorganic fillers. In order to achieve the objective of developing a proprietary paper which will reduce sidestream visibility in a full circumference cigarette, we have delineated nine major strategies. These strategies are:

1. Work with vendor to develop a more acceptable process for the manufacture of a single wrap for Superslims.

2. Optimize a magnesium carbonate (magnesite) paper for a full circumference product through the selection of type and level of fluxing agent(s) to give at least 60% sidestream reduction with minimum sacrifice in subjectives.

3. Develop low sidestream papers based on synthetic forms of magnesium carbonate or mixed magnesium carbonates including magnesite, hydromagnesite, and eitelite.

4. Develop low sidestream papers based on amorphous forms of magnesium carbonate (sol-gel process) using material which can be scaled up to produce commercial quantities.

5. Carry out studies designed to elucidate the mechanism by which magnesium carbonates and mixed magnesium carbonates achieve sidestream visibility reduction.

6. Utilize analysis of mainstream smoke, with emphasis on gas phase, to determine smoke chemistry differences between normal and reduced sidestream models in order to design filters which will result in improved subjectives.

7. Develop unique, cigarette compatible catalyst systems which will result in more complete conversion of sidestream gas phase into carbon oxides in order to reduce sidesream odor and irritation.

8. Utilize the sidestream chamber to fully characterize the analytical chemistry of sidestream smoke from appropriate reduced sidestream prototypes in conjunction with subjective evaluation.

9. Elucidate the chemistry of the pyrolysis/combustion of cigarette paper as a function of additives, temperature, etc.

Each of these strategies will be discussed below. A brief discussion of current status will be given followed by the specific tactics, along with target dates, which will be used to realize each strategy.

C. Strategies and Tactics

1. Strategy Number 1 - Optimize the single wrap for Superslims to achieve an average of 70% sidestream visibility reduction and maintain the current tar delivery target. September, October, 1991.

a. Status

A single wrap was developed for Virginia Slims Superslims utilizing high basis weight paper technology. This proprietary Philip Morris paper gives 70% sidestream visibility reduction and offers the potential for both cost and manufacturing advantages. The paper has a basis weight of ~53 g/m^2, a Coresta porosity of 10.5, an inorganic filler consisting of 27% to 33% Multifex calcium carbonate, and is coated with 10.5% mono potassium phosphate. Preliminary specifications and tolerances were established for this paper using modeling studies for chalk and phosphate levels. Mill runs made in December 1990 were used to determine the porosity spec. Currently, the base sheet is being produced in Spotswood and shipped to the Ancram mill for coating. The specifications will be finalized when the paper can be coated on line at Spotswood. The initial shipments of single wrap were made to 11.5 Coresta target, which was changed to 10.5 Coresta when factory pick-ups gave less than the desired 70% visibility reduction. QA methods for the various analyses required have been established.

The performance of the production paper has not matched that of the paper used to set porosity specifications, despite the fact that the two lots of paper showed agreement in critical paper parameters such as porosity, basis weight, and phosphate level. It is hypothesized that two papers with similar Coresta permeability could have different internal structure which could possibly affect the gas diffusional characteristics of the papers. To test this hypothesis, a study has been initiated to characterize the internal structure of paper. Two techniques are being used; mercury intrusion and oxygen diffusivity.

The mercury intrusion technique provides information on the volume intruded into the pores of various sizes. This technique has previously been used to relate the static burn rate of the cigarette to the internal pore volume of the cigarette paper. The technique appears to be reproducible in the smaller pore diameter range (<5 microns). Results obtained to date do not conclusively suggest a relationship between the mercury porosimetry data and the performance of the two Superslim papers, but they do indicate some differences. Based on a limited number of analyses, the experimental paper which gave higher puff counts and visibility reductions showed higher pore volume in the 0.1-5μ diameter pores than the production paper.

The other technique which is being explored to explain the performance of the two Superslim papers involves direct measurement of the oxygen diffusion through the paper. The instrument to be used is capable of measuring diffusion of various gases through papers and films under controlled conditions. If mercury intrusion and/or oxygen diffusion analyses suggest that the differences in the internal structure of paper could affect the cigarette performance, the critical paper parameters may have to be redefined.

There are several potential advantages to the use of a single wrap. Manufacturing is simplified without the need to run two bobbins of paper simultaneously on the maker, and the machines can be run at a higher speed. A cost reduction for material is achieved, with potential savings of 16-20 cents per thousand cigarettes, after Kimberly-Clark's final process is in place. In addition, because this paper is more porous than the previous Superslims outer wrap, perforation of the paper is no longer necessary. Consequently, the three perforators previously in use can be removed. One additional advantage was also achieved: recycling tobacco. The double wrapped cigarette could not be put through the ripper to recover tobacco.

b. Tactics and Timetables

1. Complete mercury intrusion analysis of new Superslim papers - October, 1991.

2. Obtain oxygen diffusion rate of various cigarette papers - November, 1991.

3. Initiate handsheet study to identify various papermaking process parameters that could impact the internal structures of paper - December, 1991

4. Determine why the experimental paper used to set initial porosity specifications for the single wrap burned slower than the first two millruns of production paper - Fourth quarter, 1991.

5. Evaluate single wrap containing processing aids from first on-line phosphate addition at Spotswood - September, October, 1991.

6. Test and duplicate the 10 cm^2 Coresta clamp suitable for narrow, non-porous paper - Fourth quarter, 1991.

7. Obtain additional standards suitable for General Analytical to transfer the appropriate method of analysis to QA. The new QA instrument will include monopotassium phosphate and calcium carbonate level in the analysis - October, 1991.

8. Conduct additional round-robin testing for phosphate and Coresta permeability measurements between KC and PM laboratories - Fourth quarter, 1991.

9. Evaluate single wrap for burn rate and sidestream reduction from on-line production at Spotswood. Communicate results to Kimberly-Clark - Fourth quarter, 1991.

10. Determine final acceptable tolerances in phosphate level for production papers after KC implements the use of the new size press at Spotswood - November, 1991.

c. Resource Allocations

Professionals	0.30
Technicians	0.30
Total	0.60

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2. **Strategy Number 2 - Optimize the magnesite paper for a full circumference product through the selection of type and level of fluxing agent(s) to give at least 60% sidestream reduction with minimum sacrifice in subjectives by first quarter 1992.**

a. Status

Among the most promising inorganic fillers investigated to date for reduced sidestream papers are various compositions and morphologies of magnesium carbonate. The chemistry of magnesium carbonate is complex, and many phases exist. Several crystalline phases of magnesium carbonate and mixed magnesium carbonates have been synthesized by members of the Chemical Research Division; some of these have given encouraging sidestream visibility results. The crystalline phase magnesite ($MgCO_3$) has proven most useful to date. This mineral form of magnesium carbonate is not a commercial product and it was initially examined as a synthetic material at Philip Morris. (Two patent applications on the use of magnesite are pending.) Subsequently, a natural source of excellent purity magnesite was located. Production of tonnage quantities of ground Baymag magnesite suitable for use as a paper filler has been achieved. This work involved a two-step process: (1) initial reduction in size from rocks to a coarse sand by means of impaction crushing at Industrial Crushing (Cambridge, Ohio) and then (2) final reduction in size from a coarse sand to a fine powder by processing through an impact (hammer) mill at Midwest Custom Services, Inc. (Fort Wayne, Indiana). Development of the source of magnesite and its processing and papermaking are collaborative efforts between Philip Morris and Ecusta under a confidentiality agreement.

PM representatives participated in an Ecusta paper mill run with Baymag magnesite on February 26, 1991. During the mill run ~1,000 lbs. each of four papers were produced: (a) 55 g/m^2 paper with a binary filler system (magnesite and calcium carbonate) at ~8 Coresta, (b) 55 g/m^2 paper with a binary filler system at ~5-6 Coresta, (c) 45 g/m^2 paper with a ternary filler system (magnesite, calcium carbonate and the gel form of magnesium hydroxide) at ~5-6 Coresta, and (d) 45 g/m^2 paper with a binary filler system at ~5 Coresta. The binary paper at 45 g/m^2 basis weight had only 30%, rather than the targeted 40%, total filler. A lesser amount of a 45 g/m^2 paper with a ternary filler system at a lower porosity also was produced. Ecusta has provided us with quantities of each type of paper both sized and unsized. The sized papers were treated with solutions containing tripotassium citrate and sucrose (at two different levels of potassium), perforated to 110 Coresta and cut to 26.5 mm width for the preparation of cigarettes in the Semiworks.

Two sets of cigarettes were initially made with the magnesite papers from Ecusta's mill run. Four papers were sized by Ecusta with citrate, sucrose, and, in one case, citric acid. These models gave mainstream tar deliveries ranging from 7.3 mg to 9.7 mg. The two 55 g/m^2 papers burned faster than the two 45 g/m^2 papers, while giving slightly lower tar per puff. Visibility reductions ranged from 42% to 62%. The same four base papers also were coated in-house with 6-7% potassium succinate. Cigarettes made with these papers gave higher sidestream reductions (57-67%).

Recently a number of different solutions have been sized on magnesite papers including sodium succinate, dibasic potassium phosphate, monobasic potassium pimelate, potassium succinate/pimelic acid, potassium succinate/glucose, potassium succinate/fructose, potassium succinate/monobasic potassium phosphate and potassium succinate/CMC/MAP. Although only preliminary results have been obtained with cigarette models made from these papers, some of the initial subjective evaluations have been encouraging.

A second 6,000 lb. batch of Baymag magnesite has now been ground. This filler will be used to prepare additional mill run paper at Ecusta in October, 1991. The resultant paper then will be available to prepare cigarettes for outside evaluation.

In September, 1991, a report was issued by Sue Tafur which reviews the mechanisms of sidestream reduction (PM Acc. No. 91-033). It was noted that common characteristics of reduced sidestream papers include higher basis weight and relatively low porosity. These papers are thought to function by forming a barrier to the concentrated vapor which emanates from cigarettes to form the visible sidestream smoke aerosol. The observation of heavy staining on the inside of reduced sidestream cigarette papers is consistent with barrier formation and indicates that an increased amount of smoke is condensed inside the cigarette rod. It has been hypothesized that the re-pyrolysis of additional smoke condensate within the cigarette rod may change ratios of smoke phases and hence subjective response. An investigation of this hypothesis is planned since it may help us improve subjectives for cigarettes with magnesite papers.

b. Strategies

Four strategies have been developed to achieve the objective. These strategies are:

A. Optimize current Ecusta magnesite papers with respect to sidestream reduction and subjectives by examining various paper additives.

B. Conduct development studies to optimize full-circumference cigarettes with existing magnesite papers.

C. Investigate potential improved magnesite papers.

D. Determine if increased smoke condensate within the cigarette rod is related to negative sensory attributes of cigarettes with magnesite papers.

Tactics for carrying out these strategies are outlined below.

c. Tactics and Timetable

A. **Optimize current Ecusta magnesite papers with respect to sidestream reduction and subjectives by examining various paper additives.**

1. Complete an investigation of the relationships among potassium level, sidestream reduction and subjective acceptability for currently available Ecusta papers using potassium succinate and potassium citrate (*3rd quarter, 1991*).

2. Develop analytical methods suitable for the characterization of magnesite papers with different combinations of fillers and chemical additives (*3rd and 4th quarters, 1991*).

3. Select optimum paper(s) and cation level and screen a variety of salts (monobasic potassium succinate, dibasic potassium succinate, monobasic potassium phosphate, tribasic potassium citrate, potassium gluconate, dipotassium glucose-1-phosphate, potassium and sodium acetate, tribasic sodium citrate and sodium fumarate) for subjective response and sidestream reduction. Investigate the effect of combinations of additives (e.g.

dibasic potassium succinate and monobasic potassium phosphate) (*3rd and 4th quarters, 1991*).

4. Investigate the effect of auxiliary additives such as sugars, soluble starch and acids on subjective acceptability and sidestream reduction (*3rd and 4th quarters, 1991*).

5. Examine the relationship of subjective acceptability (especially "bitterness") and pH of sizing solutions (*4th quarter, 1991*).

6. Conduct an analytical/subjective study to compare matched reduced sidestream cigarette models made with selected papers to determine if magnesite papers exhibit any characteristics which can be attributed to "bitter" taste (*4th quarter, 1991*).

B. **Conduct development studies to optimize full-circumference cigarettes with existing magnesite papers.**

1. Prepare models with 55 g/m^2 binary and 45 g/m^2 ternary papers (*3rd and 4th quarters, 1991*).

2. Select optimum tar/puff (*3rd quarter, 1991*).

3. Investigate different filter configurations (*3rd quarter, 1991*).

4. Develop flavor systems on selected model(s) (*4th quarter, 1991*).

5. Determine if the subjective evaluations of magnesite paper cigarette models are affected by "aging" (*3rd and 4th quarters, 1991*).

(a) Obtain subjective evaluations on selected "older" magnesite cigarette models which have been stored in the cold room for comparison to previous results.

(b) Conduct a subjective tracking study using magnesite cigarette models made in August and September, 1991.

C. **Investigate potential improved magnesite papers.**

1. Examine lower basis weight magnesite paper configurations (*3rd quarter, 1991, and continuing*).

2. Examine combinations and levels of inorganic fillers for magnesite papers to optimize SS reduction, ash appearance, streaking and subjectives (*3rd and 4th quarters, 1991*).

3. Prepare additional magnesite papers at the University of Maine and Ecusta (*3rd quarter, 1991, and continuing*).

D. **Determine if increased smoke condensate within the cigarette rod is related to negative sensory attributes of cigarettes with magnesite papers.**

1. Investigate the effect on subjective response of smoke condensate reapplied to cigarettes (*3rd quarter, 1991*).

2. Determine if negative subjectives can be attributed to the particulate or vapor phase of smoke (*3rd quarter, 1991*).

3. Determine if correlations exist among quantity of smoke condensate on the inside of reduced SS cigarette papers, and subjectives (*4th quarter, 1991*).

4. If results warrant additional study, identify and obtain quantitive analyses as needed and explore cigarette constructions which address subjectives issues identified in the preliminary studies (*4th quarter, 1991, and continuing*).

c. Resource Allocations

Professionals	0.60
Technicians	0.40
Total	1.00

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3. **Strategy Number 3 - Develop low sidestream papers based on forms of magnesium carbonate or mixed magnesium carbonates including magnesite, hydromagnesite, and eitelite.**

a. Status

Among the most promising inorganic fillers investigated to date for reduced sidestream papers are various types of magnesium carbonates. The chemistry of magnesium carbonate is extremely complex, and many phases exist. In addition the use of sol-gel methods (see below) permit the preparation of amorphous, or nanocrystalline, materials which have particularly interesting properties. Although these sol-gel materials appear to be the optimum forms of magnesium carbonate with regard to subjectives, a number of crystalline phases, particularly magnesite and eitelite, give reasonable subjectives using cigarettes hand-made from hand sheets, and are much easier to prepare in quantities necessary to obtain machine-made paper.

Collaboration between Philip Morris and Ecusta, under a confidentiality agreement, has led to significant progress in locating and preparing a natural source of magnesite ("true $MgCO_3$") of excellent purity for evaluation. Production has now been achieved of tonnage quantities of ground Baymag magnesite, suitable for use as a paper filler. This work involved a two-step process: (1) initial reduction in size from rocks to a coarse sand by means of impaction crushing at Industrial Crushing (Cambridge, Ohio); and (2) final reduction in size from a coarse sand to a fine powder by processing through an impact (hammer) mill at Midwest Custom Services, Inc. (Fort Wayne, Indiana). Data obtained from hand sheets using Baymag magnesite made at both Ecusta and PM have been used to specify two papers to be made in a mill run in late February at Ecusta. Both a binary filler (magnesite and calcium carbonate) and a ternary filler (magnesite, calcium carbonate, and the gel form of magnesium hydroxide) will be used. These papers will then be utilized for product development work on prototypes machine-made with magnesite papers.

Several crystalline phases of magnesium carbonate and mixed magnesium carbonates have been synthesized by members of the Chemical Research Division, some of which have given encouraging preliminary results. In particular, compounds having varying ratios of hydromagnesite to magnesium hydroxide have been prepared. The compound eitelite also has been prepared.

b. Tactics and Timetables

(1) Optimize prototypes machine-made from magnesite papers for taste characteristics (using different sizing agents, including organic acids, and different filters) in configurations that will give about 55-70% sidestream reduction - 2nd quarter, 1991.

(2) Prepare cigarette paper at the University of Maine incorporating Baymag magnesite as the sole filler - 2nd quarter, 1991.

(3) Prepare Baymag magnesite having a median particle size of less than one micron at Midwest Custom Services, Inc. for evaluation of its properties - 2nd quarter, 1991.

(4) Evaluate alternate synthesis of magnesite to determine if it can be run without contamination problems in RSA equipment - February, 1991.

(5) If the alternate synthesis can be run at RSA, make large scale run (100-200 pounds) at RSA in March, 1991. If the alternate synthesis is not appropriate, locate new facilities for synthetic magnesite - May, 1991.

(6) Pending further subjective evaluations, plan for the large-scale synthetic preparation of eitelite - 2nd quarter, 1991.

(7) Prepare co-precipitated mixtures of calcium carbonate and magnesium hydroxide/basic magnesium carbonate at atmospheric pressure. A matrix design will be utilized to examine variations in the nature and ratios of starting materials (magnesium hydroxide and calcium oxide) and other experimental conditions - 3rd quarter, 1991.

(8) Pending evaluation of sidestream visibility reductions and subjectives achieved with these fillers, plan for the large-scale synthesis of the best product from this study - 4th quarter, 1991.

(9) Prepare synthetic magnesite cigarette paper at the University of Maine and compare machine-made prototypes using these papers to prototypes made using Baymag magnesite paper - 4th quarter, 1991.

c. Resource Allocations:

Professionals	1.35
Technicians	1.75
Total	3.10

4. Strategy Number 4 - Develop low sidestream papers based on amorphous and/or nanocrystalline forms of magnesium carbonate or mixed magnesium carbonates (via sol-gel or related process) using materials and procedures which can be scaled-up to produce commercial quantities by July, 1992, and investigate new methods for the preparation of these types of compounds.

a. Status

Initial work with the sol-gel preparation of a "magnesium carbonate" using a methanolic system gave a material which, when incorporated into hand sheets followed by hand-making cigarettes, resulted in prototypes with excellent sidestream reduction and subjectives extremely close to those of a conventional cigarette. Two specific problems were encountered with this synthesis. The first was that the throughput of the procedure was quite low. Because of the limited solubility of the starting material in methanol, 100 ml of reaction mixture produced only 0.5 g of product. The second problem was encountered in making paper. Not only was the retention of this material in the paper low, but drainage times were excessively long.

A considerable amount of work has been devoted to surmounting the first of these two problems. The synthesis of a magnesium carbonate gel can now be carried out in aqueous medium, and the throughput has been improved by more than a factor of 5. Alternate routes have also been developed, both at PM and at NY Poly, which give considerably higher throughputs. We are currently in the process of evaluating many of these materials in hand-made cigarettes for both sidestream reduction and subjectives. It is expected that a few materials will be identified in the near future which can be investigated with regard to suitability for scale-up.

Approaches to solving the problems regarding making paper are now being developed. It was recently pointed out by Dr. David Kraske of the University of Maine that low retention and poor drainage are phenomena which are inconsistent. Work in the hand sheet lab tends to indicate that these materials gel on top of the hand sheet as it is being formed. This finding is consistent with the fact that cellulose is a known gelation agent. General approaches which might be attempted to solve these problems are to alter pH, increase ionic strength, form the gels in the presence of cellulose fibers, and design the synthesis of these materials to increase particle size or to decrease the size of the hydration sphere. Fundamental studies on the properties of these materials such as morphology, particle size, and zeta potentials, will have to be carried out before a choice can be made as to which approaches will be the most fruitful.

Lastly, other methods for the preparation of sol-gel type materials will be investigated, although it is likely that this work will not be initiated until early 1992.

b. Tactics and Timetable

(1) Evaluate current methods of synthesis to determine which methods lend themselves to scale up - first quarter, 1991.

(2) Evaluate properties (composition, morphology, particle size, zeta potential, paper making properties) of sol-gel particles - second quarter, 1991.

(3) Evaluate synthesized material on hand-made cigarettes for chemical and morphological constitution, sidestream reduction and subjectives - second quarter, 1992.

(4) Devise improved methods to make papers from these materials - third quarter, 1991.

(5) Initiate contact with appropriate chemical companies to begin discussions which will lead to preparation(s) of the identified material on a pilot scale - fourth quarter, 1991.

(6) Make machine made cigarettes and evaluate smoke chemistry, subjectives, and aging - date to be determined.

(7) Use alternative solvents to control particle morphology - third quarter, 1991.

(8) Modify conditions in the aqueous sol-gel route and the methyl magnesium carbonate route (temperature, reaction time) to obtain particles which have improved paper making properties - fourth quarter, 1991.

(9) Examine aging effects on the particles and on the papers made using these particles - third quarter, 1991.

(10) Examine spray drying to obtain particles - first quarter, 1992.

(11) Continue development of analytical techniques to characterize sols, gels, particles, and paper compositions - continuing.

(12) Examine filler and filler/fluxing agent and filler/fluxing agent/paper systems to determine the effects caused by thermal treatments - fourth quarter, 1992.

c. Resource Allocations

Professionals	5.10
Technicians	1.05
Total	6.15

5. Strategy Number 5 - Carry out studies designed to elucidate the mechanism by which magnesium carbonates and mixed magnesium carbonates achieve sidestream visibility reduction.

a. Status

The understanding of mechanisms of sidestream reduction continues to be incomplete. In order to provide a basis for further work in this area, the status of proposed hypotheses, relevant data, and ideas or speculations concerning possible mechanisms was recently compiled in a special report (Accession #91-033). The proposed hypotheses were placed into five categories and a general consensus for refuting or agreeing with the specific type of proposal was given.

To date, experimental work related to sidestream reduction mechanisms has been limited. Recent studies using the Sidestream

Chamber have shown smaller particle sizes in the aerosol from low sidestream cigarettes. A correlation has been found between particle size and sidestream smoke particulates (TEOM) as measured in the chamber, but smaller aerosol particles cannot account for reduced sidestream visibility as measured by light scattering.

A number of hypotheses have been developed regarding the mechanisms possible for reducing sidestream smoke or influencing subjectives. The hypotheses are framed to provide an understanding of what is really happening to the smoke mass in low sidestream cigarettes and then to answer the question of how. The hypotheses and a brief description of the approaches to be used in addressing each of these are given below:

Hypothesis 1. Some of the sidestream smmoke in low sidestream cigarettes is allocated to mainstream either intact or thermally cracked.

The smoke mass allocation in low sidestream models over a range of porosities, will be measured using radiolabelled tobacco/tracer, neutron radiography, and analytical techniques. Detailed qualitative and quantitative analyses of mainstream and sidestream TPM and gas phase will be obtained and compared with data on standard cigarettes.

Hypothesis 2. Low sidestream papers force sidestream smoke closer to the thermal plume thereby causing some cracking of smoke.

Magnified video images of the smoke plume and Schlieren imaging of the thermal plume, as well as smoke aerosol particle size measurements will be made on low sidestream models containing a variety of fillers and compared with each other as well as with standard cigarettes.

Hypothesis 3. Paper porosity or transient changes in paper permeability at or near the char line is the dominant mechanism of sidestream smoke reduction.

Experiments will be designed to measure changes in paper porosity/permeability with changes in temperature as well through deposition of condensibles.

Hypothesis 4. Excessive smoke condensation on paper of low sidestream cigarettes is affected by thermal properties of the filler.

Thermal properties, e.g., thermal conductivity and heat capacity of several fillers will be correlated with the quantity of smoke condensate in the paper within a narrow porosity range. Quantity of smoke shall be tracked analytically as well as through neutron radiography.

Hypothesis 5. Sidestream smoke reduction results from thermal (homogeneous vapor phase) and/or catalytic (heterogeneous by tobacco char/ash and filler) cracking of newly formed tars during devolatilization of tobacco.

Fresh tar will also be generated by devolatilization of tobacco and characterized by molecular weight distribution and aerosol formation. The rate and extent of tar cracking as a function of time, temperature, type of catalysts will be determined.

Hypothesis 6. The function of sizing additives in magnesium carbonate low sidestream papers is to provide sintering (cohesion of one particle to another) which leads to ceramic formation.

The thermal behavior and associated physical changes of (a) sizing additives individually, (b) additives plus filler, and (c) additive plus filler plus cellulose, i.e., sized papers, will be determined utilizing high temperature metallurgical hot-stage and reflectance microscope, TGA/DTA/MS, X-ray diffraction, BET surface area, and SEM.

Hypothesis 7. Morphology/chemical composition or surface area of filler (paper) play a role in sidestream reduction.

Examination of in situ changes in morphology, i.e., particle size and shape of filler, occurring in papers in the course of combustion, with correlation to the nature of the filler and sizing agents will be undertaken. Fillers will include both, calcium carbonates and magnesium compounds of different morphologies.

Hypothesis 8. Increased smoke condensate in the cigarette rod is responsible for the negative sensory attributes of cigarettes with magnesite papers.

Smoke condensate on paper will be extracted and reapplied to cigarettes to evaluate subjective response. Determine whether negative subjectives can be attributed to the particulate or vapor phase of smoke and whether correlations exist among quantity of smoke condensate on the inside of magnesite cigarette papers, porosity, sidestream reduction, and subjectives.

b. Tactics and Timetable

(1) Organize experimental approaches for investigation of proposed mechanisms and identify the resource requirements - fourth quarter, 1991.

(2) Determine whether condensible organics reduce paper porosity in the vicinity of the char-line - first quarter, 1992.

(3) Measure physical properties and chemical composition of sidestream smoke generated by static burn for mined magnesite models and standard cigarettes using the environmental chamber - first quarter, 1992.

(4) Study, by analytical microscopy, the change in morphology and chemical composition (phase changes) of experimental magnesium carbonate/magnesium hydroxide filler materials before and after addition to cigarette paper - first quarter, 1992.

(5) Use imaging techniques, i.e., video, Schlieren, neutron radiography, and IR camera to compare low sidestream and standard models with respect to location of thermal and aerosol plumes, and evidence of vapor condensation within the paper and cigarette rod - mined magnesite models - first quarter, 1992; other models, continuing, as they become available.

(6) Extract and characterize condensibles from the inside of magnesite papers, apply the extract to standard cigarettes, and evaluate subjective responses. Correlate quantity of smoke condensate with sidestream reduction, paper porosity, and subjectives. - second quarter, 1992.

(7) Determine the mechanistic function of sizing additives in magnesium carbonate papers - second quarter, 1992.

(8) Examine in situ changes in morphology occurring in papers in the course of combustion, with correlation to the nature of the filler and sizing agents - third quarter, 1992.

(9) Determine which properties of filler, e.g., morphology, surface area, heat capacity, thermal conductivity, etc. affect sidestream smoke - third quarter, 1992.

(10) Determine detailed chemical composition of MS and SS gas phase and TPM for low sidestream models and compare with data previously accumulated - third quarter, 1992.

(11) Determine mass allocation of total smoke in low sidestream cigarettes under static and dynamic conditions by analytical and radiochemical techniques - third quarter, 1992.

(12) Model compounds found in smoke as well as freshly generated tar will be submitted to thermal and catalytic cracking to determine the extent of cracking as a function of time, temperature, and type of catalyst to delineate whether sidestream smoke reduction results from homogeneous or heterogeneous catalysis. - fourth quarter, 1992.

(13) Determine the occurrence and possible consequences of transient changes in paper permeability at or near the char line - fourth quarter, 1992.

(14) Review and analysis of data to support or refute hypothesis and validate supported hypotheses - continuing

c. Resource Allocations

Professionals 6
Technicians 1

Total 7

6. **Strategy Number 6 - Utilize analysis of mainstream smoke, with emphasis on gas phase, to determine smoke chemistry differences between normal and reduced sidestream models in order to design filters which will result in improved subjectives.**

a. Status

Problems with subjectives continue to plague the low sidestream effort. Analyses to date have failed to identify any compound, or classes of compounds, responsible for inferior mainstream subjectives. An empirical approach to the problem is to design filters which will selectively remove certain chemical classes and evaluate these filters on low sidestream cigarettes. Two approaches are being investigated, both based upon the finding that charcoal often improves mainstream subjectives from low sidestream models. The first is to compare models with charcoal to models with CA filters both subjectively and analytically, and to investigate models where the charcoal filter has been chemically modified. A current study is utilizing fifteen cigarette models with eight different filters using both conventional and low sidestream cigarette wrappers. The filter constructions include cellulose acetate, charcoal, and paper filter materials, some with acidic or basic additives. A model with ART filler is also being tested. Mainstream smoke particle size analyses were completed, and no differences were noted in average particle size for the different filter materials. Fractionation of mainstream smoke into acidic, basic, and neutral fractions is being used to obtain relative smoke component deliveries for 200 mainstream smoke compounds. Panel testing has been completed for the models, and the results will be statistically correlated with the smoke component deliveries.

The second approach is to attempt to develop a high surface area material which can be applied to a filter web in solution form. This approach is of particular interest for Virginia Slims Superslims, since a slim charcoal filter would be prohibitively expensive. One promising source of a soluble material which will leave a high surface area residue when the solvent evaporates are the sol-gel derived oxides and carbonates already being investigated for low sidestream papers.

In addition, further studies of smoke chemistry as a function of paper type should be carried out. Detailed compositions of the acidic, basic, and neutral fractions of mainstream smoke condensate for fifteen cigarette models made with conventional and low sidestram wrappers and several different filters were examined by severam statistical approaches. Comparisons of models made with a conventional paper and a low

sidestream calcium carbonate wrapper show significant shifts in many of the 183 major peaks which were examined. Liking ratings by panelists also show significant differences for the two different wrappers. As of yet, no specific individual components can be isolated as having a determinate effect on the subjective performance of the papers. This analyses will serve as a baseline for comparing low sidestream papers containing magnesium fillers to low sidestream calcium carbonate papers which will be carried out in 1992.

b. Tactics and Timetable

(1) Identify promising sol-gel derived materials for use in fabricating modified filters - March, 1992.

(2) Develop techniques for the application of sol-gels to filter materials - second quarter, 1992.

(3) Test modified filters subjectively and analytically - third quarter, 1992.

(4) Conduct detailed mainstream smoke condensate analyses of low sidestream cigarettes made with a magnesium carbonate paper, a magnesium hydroxide paper, and a calcium carbonate paper - March, 1992.

c. Resource Allocations

Professionals	0.35
Techicians	-
Total	0.35

7. Strategy Number 7 - Develop unique, cigarette compatible catalyst systems which will result in more complete conversion of sidestream gas phase into carbon oxides in order to reduce sidestream odor and irritation by 1995.

a. Status

Although considerable progress has been made directed toward the reduction of sidestream visibility, none of the systems investigated to date has a major obvious effect on sidestream gas phase. Since it is most likely the gas phase which contains those components responsible for sidestream odor and irritation, new techniques must be utilized to address this problem. Work on low sidestream and conventional cigarettes using

the sidestream chamber will begin to provide us with some information as to the nature of those gas phase components which are responsible for odor and irritation (see below). However, it is not an unreasonable assumption that compounds such as low molecular weight aldehydes, ammonia, and low molecular weight amines are involved. Conceptually, the most effective method to reduce the concentration of such compounds in sidestream smoke would be to incorporate a catalyst of some type in cigarette paper which would result in either oxidizing these compounds to less odorous materials, or ideally to carbon dioxide. This approach will require considerable time and effort.

b. Tactics and Timetable

(1) Invite outside scientists, expert in the field of catalysis, especially as it relates to this strategy, to visit PM R&D and to present technical seminars - June, 1992.

(2) Ask PM R&D personnel expert in this area to present seminars related to catalysis and paper technologies - June, 1992.

(3) Obtain, organize, and evaluate literature and PM information on catalysis in the cigarette area which may be related to paper technologies - June 1992.

(4) Expand R&D staff to include an individual who has proven expertise in catalysis, especially in areas related to this strategy - 1992.

(5) Develop a list of possible target approaches - 1992.

(6) Organize a group of chemists, physicists, and other scientists to provide experimental and theoretical effort - 1992.

(7) Initiate experimental work - 1993.

(8) Evaluate initial results, plan future work, etc. - 1993.

8. Strategy Number 8 - Utilize the sidestream chamber to fully characterize the analytical chemistry of sidestream from appropriate reduced sidestream prototypes in conjunction with subjective evaluation.

a. Status

The sidestream chamber continues to expand in capability. Recent additions include an on-line infrared gas analyzer for determination of

mainstream carbon monoxide and carbon dioxide in conjunction with normal sidestream collections, and an aerosol dilution device to facilitate determination of sidestream particle size distributions. A study to determine confidence levels in the information generated by the aerosol instruments has begun by conducting repeated measurements on IM13 cigarettes. Interesting data have been generated showing, for the first time, differences in particle size distributions for reduced visibility cigarettes versus conventional controls. Evaluation of the change from double to single wrap for Trim is currently underway by conducting multiple chamber runs to compare prototypes of the two models. Initial planning has begun to modify the chamber to facilitate normal analytical data generation simultaneous with sidestream subjective evaluations. An O.I. Analytical and Hewlett-Packard headspace/gc/ms system has been received and initial installation completed. This multi-component system will be used for trapping and identification of additional sidestream materials from chamber runs.

b. Tactics and Timetables

(1) Complete smokings of Trim single wrap test model versus Trim double wrap control. Analyze data and summarize in memo format - March, 1991.

(2) Become familiar with and devise protocols for collection and analysis of selected chamber smoke components utilizing the recently installed headspace/gc/ms system - second quarter, 1991.

(3) Conduct analysis of selected sidestream smoke components utilizing the headspace/gc/ms system and compare cigarette models with reduced visibility to appropriate controls - second quarter, 1991.

(4) Devise and implement on-line methods for collection of smoke directly into adsorbent tubes for automated analysis utilizing the headspace/gc/ms system - third quarter, 1991.

(5) Investigate the availability of new instrumentation for measurement of smaller sidestream smoke particle sizes than currently possible with in-house analyzers. Submit appropriate requests for purchase - second quarter, 1991.

(6) Examine additional aerosol instrumentation for potential chamber incorporation - third quarter, 1991.

(7) Construct an improved sidestream smoke dilution device for determination of sidestream smoke particle size distributions - September, 1991.

(8) Study the behavior of smoke aerosols over extended time periods and construct a data base of aerosol information on IM13 controls and selected cigarette models - continuing.

(9) Initiate a new program to monitor sidestream analyticals while simultaneously conducting subjective evaluations in February, 1991. This new program includes:

(a) Evaluate various means for conducting subjective evaluations on sidestream smoke external to the sidestream chamber on cigarettes smoked within the chamber - March, 1991.

(b) Modify the sidestream chamber door to facilitate sidestream subjective studies - March, 1991.

(c) Determine the appropriate number of cigarettes to yield valid subjective data as well as appropriate analytical data - April, 1991.

(d) Utilize the seven models defined for this study to determine sidestream subjectives simultaneous with collection of sidestream and selected mainstream data - second quarter, 1991.

(e) Conduct normal 30 cigarette (5 cigarette aerosol) runs to generate sidestream and selected mainstream data - second quarter, 1991.

(10) Determine experimental conditions necessary for the collection and quantitation of acrolein from cigarettes smoked within the sidestream chamber. Utilize this procedure to monitor selected cigarette models for sidestream acrolein - third quarter, 1991.

(11) Determine experimental conditions necessary for the puff-by-puff quantitation of nicotine generated in sidestream smoke. Utilize this procedure to determine puff-by-puff nicotine from selected cigarette models - third quarter, 1991.

(12) Investigate the feasibility of utilizing an on-line total sulfur analyzer in the sidestream chamber. Install and operate if shown to be effective - fourth quarter, 1991.

c. Resource Allocations

Professionals	3.20
Technicians	0.80
Total	4.00

9. Strategy Number 9 - Elucidate the chemistry of the pyrolysis/combustion of cigarette paper as a function of additives, temperature, etc.

a. Status

The results of a Box-Behnken study conducted with the Solar Energy Research Institute (SERI) quantified the effect of potassium ion concentration, pH, and pyrolysis temperature on cellulose and paper pyrolysis product distribution. Differences in the product mix resulting from different additives to papers are believed to affect subjectives. The work was done using molecular beam mass spectrometry to evaluate the pyrolysis and combustion product mix for flax samples and high basis weight paper samples to which three levels of mono potassium phosphate were added at three pH levels (3, 4.4, and 9). The pH 9 level is equivalent to dipotassium phosphate. Results showed that three main product slates were a direct function of pH, potassium ion concentration, and temperature. These three principal classes of compounds are anhydrosugars, carbonyl compounds, and furan-type compounds. The data generated to date by this work are considered by patent counsel to be sufficient to support our patent claims for PM 1393. This patent is for the high basis weight paper which will be used for the single wrap Virginia Slims Superslims. Additional data also indicate that there is an interaction between the phosphate and the calcium carbonate which affects the products formed when the paper is burned or pyrolyzed. The effect depends on the amount of oxygen present.

b. Tactics and Timetable

The following outline gives a brief description of the work to be done at SERI in 1991-1992. Samples will be provided by Philip Morris. Pyrolysis-mass spectral analyses and data reduction by multivariate analyses will be performed at SERI.

(1) Pyrolysis and combustion of selected paper samples using temperatures ranging from 480-650°C - second quarter, 1991.

(2) Pyrolysis and combustion of phosphate treated papers at different oxygen levels - second quarter, 1992.

(3) Perform collision induced decomposition on selected nominal m/z values of interest under conditions of particular interest as determined jointly by PM and SERI researchers - third quarter, 1992.

(4) Quantitate selected compounds from key experiments - third quarter, 1992.

(5) Evaluate the effect of divalent metal ions on the pyrolysis and combustion of selected flax and paper samples - third quarter, 1992.

(6) Analyze model compound in "cracking" study molecular beam mass spectrometry - fourth quarter, 1992.

(7) Carry out detailed studies of the pyrolysis of ^{13}C-labelled cellulose in order to elucidate the mechanism of its pyrolysis under conditions relevant to cigarette paper pyrolysis - first quarter, 1992.

c. Resource Allocations

Professionals	0.50
Technicians	0.20
Total	0.70

D. Resource Allocations for Reduced Sidestream

Professionals	11.55
Technicians	4.65
Total	16.20

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III. Papers to Control Ash Flaking and Puff Count

A. Objective - To design a cigarette paper which will control ash flaking on ultra low delivery cigarettes and give low puff counts without the need to apply high citrate levels. Completed March 1991.

B. Introduction and Status

The design of low delivery cigarettes, such as BOLD and Marlboro Ultra Lights, has previously required the use of a high porosity paper with high levels of citrate (about 2.5%). It has been established that the use of high citrate levels results in increased ash flaking while the cigarettes are being smoked. In addition, even with a paper with a Coresta porosity of 46, and 2.5% citrate, the BOLD prototypes are still about one-half puff more than target. Work on the low sidestream program had indicated that increasing basis weight would decrease puff count, and possibly decrease ash flaking as well. Further work demonstrated that going from a basis weight of 25 to 30 g/m^2 on Marlboro Ultra Light enabled puff counts and tar delivery to be matched with the control with 1% citrate instead of 2.5% citrate. The higher basis weight model appears to have no ash flaking problem, and preliminary subjective screening has been promising to date.

Both calcium carbonate level and the ratio of sodium to potassium citrate have also been evaluated as to their effect on puff count. Increasing calcium carbonate reduces puff count. This finding is of considerable importance to the BOLD program, since our suppliers routinely use low calcium carbonate levels in high porosity papers. It was demonstrated that a 25 g/m^2 basis weight paper with 1.7% citrate and 36% calcium carbonate at 46 Coresta will meet the target puff count in a BOLD configuration. Increasing calcium carbonate levels also will decrease ash flaking. This point is still being studied. Sodium to potassium citrate ratio, on the other hand, had no measurable effect on puff count.

Lastly, the effect of Multifex chalk was investigated. Although there was a definite decrease in puff count when equal levels of Albacar chalk were compared to Multifex chalk, all evaluations to date on BOLD indicate that the Albacar models are subjectively preferred.

There were two major strategies which were being pursued to accomplish the objective for this part of the program. These were:

1. Evaluate papers with varying basis weights, calcium carbonate levels, and citrate levels in order to relate these parameters to puff count, and designate optimum papers for BOLD and Marlboro Ultra Lights.

2. Carry out studies relating the effect of basis weight, calcium carbonate levels and citrate levels to ash flaking in order to design papers for ultra low delivery cigarettes with reduced ash flaking.

Each of these strategies will be discussed in detail below.

C. Strategies and Tactics

1. Strategy Number 1 - Evaluate papers with varying basis weights, calcium carbonate levels, and citrate levels in order to relate these parameters to puff count, and designate optimum papers for BOLD and Marlboro Ultra Lights.

a. Status

Initial BOLD prototypes made had not achieved the desired puff count using conventional design methods. Information obtained regarding cigarette papers from the reduced sidestream program has provided three additional approaches to reducing puff count; namely, increasing the basis weight of the papers, increasing the calcium carbonate content of the papers, and increasing the potassium to sodium ratio for the citrate sizing. Moreover, there is also evidence to indicate that replacing Albacar with Multifex chalk results in a decreased puff count. Two years ago, sufficient data existed to qualitatively substantiate these conclusions, but we had no in-house data to be able to establish the quantitative relationship of any of the above parameters to puff count, particularly in dealing with conventional cigarette papers. An early study was run using papers with basis weights of 25, 30 and 35 g/m^2 at 35 Coresta porosity sized with three levels of citrate (0, 1, and 2.5% with a 2.8:1 sodium to potassium ratio). These papers were used to make cigarettes to Marlboro Ultra Lights specifications except for the papers. This study established the quantitative relationship of basis weight with puff count, and showed that a cigarette with a 30 g/m^2 basis weight paper with 1% citrate was essentially identically matched with respect to FTC tar delivery and puff count to a model with 25 g/m^2 paper sized with 2.5% citrate.

Two additional studies were conducted. The first utilized a series of 22 papers at three different basis weights (25, 30 and 35 g/m^2), with three different levels of both Albacar and Multifex calcium carbonate (25, 30, and 36%), and two different levels of citrate (2.5 and 1.7% with a 2.8:1 sodium to potassium ratio). These papers were used to make cigarettes to BOLD specifications, and puff count and tar data were obtained on weight and ventilation selected cigarettes. The conclusions

from this study showed that increasing calcium carbonate decreases puff count, increasing basis weight decreases puff count, and substituting Multifex for Albacar chalk also decreases puff count. Subjective screening to date indicates that there does not appear to be a subjective penalty incurred by increasing calcium carbonate level. Two patent applications were filed in April 1991 related to the specially designed papers which resulted from these studies.

PM 1570 covered the use of high chalk papers for use in optimizing the puff count of low delivery cigarettes. PM 1596 covered the use of fine particle size chalk in cigarette paper to accelerate the burn rate in high or low delivery cigarettes.

The paper which was successfully developed for Project BOLD was a 28 g/m^2 paper with 35% calcium carbonate, 1.7% sodium/potassium citrate, at 46 Coresta porosity. A follow-up study of the effect of porosity from 37 to 50 Coresta on BOLD models showed little effect on puff count over this range. This is apparently in the flat region of the puff count - porosity curve.

This paper has already been introduced commercially on two cigarette brands, Cambridge and Bristol Lowest. It will also be used on the 1mg product which will be introduced in Europe October 1, PM Lights Extra.

b. Tactics and Timetables

(1) Obtain factory prepared Marlboro Ultra Lights Models - October 1991.

(2) Determine feasibility of replacing 46 Coresta 1.7 and 2.6% citrate papers on other models - November 1991.

c. Resource Allocations

Professionals	0.50
Technicians	0.05
Total	0.55

2. Strategy Number 2 - Carry out studies relating the effect of basis weight, calcium carbonate levels and citrate levels to ash flaking in order to design papers for ultra low delivery cigarettes with reduced ash flaking.

a. Status

Ultra low delivery cigarettes with high ET content tend to flake more than normal cigarettes. There are two reasons for this. The first is a consequence of the blend itself. High ET blends form a less dense ash on smoking which results in a total ash - tobacco and paper - of lower integrity than from a cigarette containing a normal blend. The second is that current PM ultra low delivery cigarettes contain high levels of citrate which contributes to the problem. Possible approaches to eliminating this problem through redesigning the cigarette paper were to: 1) increase the basis weight of the paper; and 2) utilize a higher surface area chalk. Encouraging results have been obtained with both of these approaches. The second approach may be problematical. Substituting Multifex chalk for Albacar chalk at equal porosities and basis weights results in a paper with lower tensile strength. Nevertheless, further work may be appropriate since this approach gave the best ash characteristics, based on a dynamic ash evaluation test. This test can provide reproducible and quantitive evaluations for ash cohesiveness and was developed for use on the five port smoker. Ratings obtained in this manner in blind testing were reproducible and showed that both the fine particle size chalk and increased levels of the standard Albacar chalk give improved ash cohesiveness. Increased basis weight also improves the ash. These findings were used to file a patent for papers and cigarettes for improved ash characteristics, PM1518. The optimized paper (the same as for BOLD) will be evaluated on other cigarette brands with ash flaking problems.

b. Tactics and Timetables

(1) Evaluate factory made MFUL cigarettes made with 28 g/m^2 papers for ash flaking - October 1991.

(2) Apply technology to Merit Ultra Lights - Fourth quarter, 1991.

c. Resource Allocations

Professionals	0.40
Technicians	0.10
Total	0.50

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D. Resource Allocations for Papers for Control of Puff Count and Ash Flaking

Professionals	0.90
Technicians	0.15
Total	1.05

IV. Project Tomorrow

A. Objective - To develop procedures for the application of transverse bands to cigarette paper in order to control burn rate by January, 1993.

B. Introduction and Status

It was shown some time ago that a Kimberly-Clark patented paper made by affixing small bands of a dense paper to normal cigarette paper resulted in cigarettes which would self-extinguish when the char line reached the band. There are many problems associated with this concept, however, particularly problems in making the paper at high speed, and the effect of such paper on current cigarette making machines. As a consequence, several approaches have been looked at to apply some type of transverse bands to cigarette paper. One such approach is the "daubing dandy." The original daubing dandy concept consisted of a modified dandy roll designed to apply intermittent layers or bands of cellulose across the wet base web on a paper machine. The concept was reduced to practice at the University of Maine, and papers were prepared there using both hardwood pulp, Cellulon, and Buckeye "expanded fiber." Cigarettes were produced with the hardwood banded paper which exhibited the desired burn rate control. Because of the mechanical complexities involved in wet-end modification of a paper machine, support was obtained from PM Engineering to scale up the daubing dandy concept. Most recently, Beloit Corporation has been contacted to design an approach suitable for achieving this objective. A patent application, PM 1429, was filed in November, 1990.

A second approach is the application of a cellulosic material to the paper off-line through the use of a rotogravure-type printing technique. AVICEL, a microcrystalline cellulose, was successfully applied using CMC as a binder with a modified rotogravure roll. Two other materials, Cellulon and Buckeye's "expanded fiber," have also been investigated. Due to the unique properties of these materials, they have the ability to bind to paper without an adhesive. Because of their fibrous character, however, they require modification in order to apply a rotogravure-type technique. Extrusion-type, spray or ink jet techniques have been found to be suitable for processing these materials, and the appropriate equipment has been evaluated. Patent application PM 1479 was filed in September 1991. Commercialization efforts with Kimberly-Clark are under way.

The last approach investigated involved the application of calendered bands to the paper before it is completely dry. Patents have previously been issued claiming calendered bands on dry paper. However, in order to achieve a measurable effect on burn rate, the paper must be calendered at least four times. Since wet paper is far more compressible than dry paper, that approach was studied for feasibility but has been abandoned.

As is obvious from the above discussion, there are two major strategies still being pursued by the Paper Technology Program for Project Tomorrow. These are:

1. Design and construct modifications to a paper making machine which will allow the application of cellulosic bands to paper at or near the wet end.

2. Explore the application of bands of cellulose to cigarette paper using either rotogravure or extrusion-type techniques.

Each of these strategies will be discussed in detail below.

C. Strategies and Tactics

1. Strategy Number 1 - Design and construct modifications to a paper making machine which will allow the application of cellulosic bands to paper at or near the wet end.

a. Status

The initial evaluation of a rotogravure type band application positioned above the couch roll on Beloit's pilot paper machine was partially successfully. Band contrast was acceptable, the bands remained intact through the press section, and the device did not interfere with the operation of the paper machine. Unfortunately the level of application was low and uniformity within the banded region was unacceptable.

Two major modifications were made to the rotogravure system. The banded section on the rotogravure roll has been ground with noncontinuous grooves which should restrict the blade from dipping into the grooves. This should increase application level. The addition of 1% CMC (based on Cellulon) to the slurry (a 1% mix of homogenized Cellulon) improves flow and agglomeration characteristics. This modification should improve band uniformity. In addition a florescence dye has been developed for use as a tracer to determine the level of application.

Exploratory work at Bryce-Jewett under the supervision of PM Engineering resulted in a development of a slurry application device (moving orifice) that can apply bands by spraying slurry (1% homogenized Cellulon). The moving orifice has been successfully operated at production speed by spraying on a moving belt. Both the rotogravure applicator and the moving orifice will be evaluated at Beloit in October 1991.

b. Tactics and Timetables

(1) Modify the rotogravure coater as required to produce acceptable banded paper - December, 1992.

(2) Evaluate the moving orifice application device at Beloit - December, 1991.

(3) Assist PM Engineering in the evaluation of these units - December, 1991.

c. Resource Allocations

Professionals	0.75
Technicians	0.75
Total	1.50

2. Strategy Number 2 - Explore the application of bands of cellulose to cigarette paper using either rotogravure or extrusion-type techniques.

a. Status

Colloidal cellulose - In this concept bands of cellulosic material are applied transversely to the dry paper by a rotogravure-type printing technique. The cellulosic material used is a form of microcrystalline cellulose of very fine particle size (0.2 μ). This material, AVICEL CL-611, is co-processed with CMC, which serves to stabilize the colloidal suspension. A modified gravure roll was designed in conjunction with Filter Development. This roll demonstrated the ability to transfer bands of the colloid to the substrate in varying levels. Up to 13% concentration levels were achieved in the bands. On 137-1 paper, about 3.5% addition level in the bands achieves the desired objective. A patent application, PM 1479, has been filed. A confidentiality agreement with Kimberly-Clark has been obtained, and further work with the material will be done in conjunction with KC.

In related experiments, cigarettes which already show some reduced burn rate were hand-painted with different levels of the colloidal material. Using propyl paraben as a tracer, it was found that application levels of 3, 1.5, and 0.4% of the colloid were effective at obtaining further burn rate control. Electron microscopy work showed that the fibrous materials form a dense mat on the surface of the paper web, providing a region in which burn rate is inhibited.

Cellulon - As was pointed out above, both Cellulon and Buckeye's "expanded fiber" have the ability to bind to paper without an adhesive. Further development work is planned with Cellulon, once a cleaner material has been developed. Work with "expanded fiber" is on hold.

b. Tactics and Timetable

Colloidal Cellulose (Avicel)

(1) Obtain coated papers at two different porosities with different levels of application, and different band width and spacing of bands - Fourth Quarter 1991.

(2) Prepare cigarettes with these papers with conventional cigarette configurations - January 1992.

(3) Evaluate cigarettes for zone-specific burn rate modification and working with Product Development USA, optimize cigarettes - Second Quarter 1992.

Cellulon

(1) Continue work with "Ryder-roll" - Fourth Quarter 1991.

(2) Obtain PM cleaned Cellulon and other samples for biological studies - Fourth Quarter 1991.

(3) Negotiate exclusivity on uses of cleaned Cellulon for Philip Morris - Fourth Quarter 1991.

(4) Obtain machine-made papers with appropriate levels of cleaned Cellulon in bands - March 1992.

(5) Prepare cigarettes from machine coated material - April 1992.

(6) Evaluate cigarettes for burn rate modification and determine if more work should be done with this approach - June, 1992.

(7) If accepable, proceed toward commercialization.

c. Resource Allocations

Professionals	0.80
Technicians	0.40
Total	1.20

V. Cigarette Paper Specifications

A. Objective - To determine those cigarette paper parameters which effect cigarette specifications and manufacturing processes and set meaningful specifications and tolerances for cigarette papers.

B. Introduction and Status

At present cigarette paper specifications can be divided into three separate types: 1) parameters which affect cigarette performance, e.g., paper porosity; 2) properties which affect cigarette making, e.g., tensile strength; and 3) properties which affect cigarette appearance, e.g., paper opacity. Recent studies have shown that there are at least four paper properties which affect cigarette performance; namely, porosity, level of citrate, level of calcium carbonate, and basis weight. Although we have specifications for all of these, only two of them - porosity and basis weight - are routinely monitored. Calcium carbonate was not defined as a critical parameter. Moreover, studies had not been carried out to establish appropriate tolerances to ensure that cigarette deliveries and puff counts are within specifications. In the case of calcium carbonate level, the importance not was not previously known. The studies discussed below will provide information for establishing meaningful paper specifications.

The goal of the experiment was to determine the effects of physical paper properties on the performance of cigarettes, particularly in terms of tar delivery and puff count. The properties of interest were basis weight, chalk content, porosity, and citrate level. If we had evaluated three levels of each parameter, the total number of combinations would have been unmanageably large. Since it was known that interactive effects could be accounted for through experimental design, John Tindall's help was enlisted in recommending a set of combinations to give valid results without having to use all the possibilities in making cigarette models.

The cost of making all papers for the design would have been prohibitive. Consequently, an inventory of papers that were readily available from Kimberly-Clark served as the starting point around which the experiment was designed.

The basis weight ranged from 25 to 35 grams per square meter; the chalk content ranged from 25 to 37%; the porosity ranged from 13 to 46 CORESTA; and the citrate level ranged from 0.6% to 2.6%. The effect of using Multifex chalk was also investigated. Of the 33 papers, Kimberly Clark had base papers available for 24, and only had coating with the appropriate level of citrate was required. Kimberly-Clark made five mill runs and coated them to give the remaining nine papers.

Samples of each paper were submitted to ARD for Ca content, from which chalk level was calculated, and to CI for citrate level. The basis weight and porosity were measured for each paper by Cigarette Technology personnel. After cigarettes were made with the papers, samples were resubmitted for all the physical testing, so we would be certain of the attributes of the paper on the cigarettes. Cigarettes were then made in the R&D Semiworks from each paper to Marlboro KS construction. The somewhat surprising result of this study was that the chalk level affects tar delivery as much as the porosity of the paper.

At the lowest chalk level allowed by the spec, 24%, the program predicts the tar delivery will be 16.5 mg, within the range of the one-week average. At the highest level, 37%, the predicted tar delivery is 15.3 mg, below the lower tar limit for one-week or running eight-week averages.

The two strategies which will be pursued to continue these evaluations are:

1. Evaluate the effects of paper properties on cigarette performance attributes (puff count, tar, static burn time, etc.) in order to determine whether tolerances on paper specifications are appropriate for Marlboro or other full flavor cigarettes, including determination of paper uniformity requirements for the product.

2. Evaluate the effects of paper properties on cigarette performance attributes (puff count, tar, static burn time, etc.) in order to determine whether tolerances on paper specifications are appropriate for low delivery cigarettes.

Each of these strategies will be discussed in detail below.

C. Strategies and Tactics

1. Strategy Number 1 - Evaluate the effects of paper properties on cigarette performance attributes (puff count, tar, static burn time, etc.) in order to determine whether tolerances on paper specifications are appropriate.

a. Tactics and Timetable

(1) Present results of study to an interdepartmental group for discussion. September, 1991.

(2) Test the model, using different or production papers. fourth quarter 1991.

(3) Provide information to B. Carter for Fast Flow program - September, 1991.

(4) Obtain pallet uniformity requirements for Marlboro wrapper. October, 1991.

(5) Based on recommendations, propose changes required of vendors. November, 1991.

(6) Prepare and publish report - first quarter, 1992.

(7) Negotiate appropriate changes, if any, with vendors. second quarter 1992.

b. Resource Allocations

Professionals	0.75
Technicians	.10
Total	0.85

2. Strategy Number 2 - Perform the same evaluations for low delivery cigarettes using Marlboro Ultralights as the cigarette prototype.

a. Tactics and Timetable

(1) Submit cigarette requests - November, 1991.

(2) Obtain CI data - December, 1991.

(3) Evaluate data statistically. January, 1992.

D. Resource Allocations for Specifications Project

Resource Allocations

Professionals	0.75
Technicians	.25
Total	1.00

VI. Improved Tipping Papers

A. Objectives - Develop improved tipping papers to reduce potential customer complaints by December, 1991.

B. Introduction and Status

Current tipping papers are still subject to at least two quality problems on an occasional basis; namely, filter flare-up and lip release. Initial work with cork-on-white tipping has established that using defined levels of low silicate inks appears to eliminate the filter flare-up problem. Work is ongoing to qualify such tipping papers. Some success has been achieved improving lip release properties of white tipping. This has been accomplished by double coating the tipping paper with nitrocellulose. However, the improvement is perhaps only marginal. If substantial improvements cannot be made with current "hold out" agents, research work on new materials to take the place of nitrocellulose will have to be initiated.

The two strategies being pursued to accomplish the objective are:

1 Modify cork-on-white tipping to eliminate filter flare-up through the use of defined levels of low silicate inks by June, 1991.

2. Modify white tipping papers to improve lip release properties by December, 1991.

Each of these strategies will be discussed in detail below.

C. Strategies and Tactics

1. Strategy Number 1 - Modify Cork-on-white tipping to eliminate filter flare-up through the use of defined levels of low silicate inks.

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a. Status

Based on a very low complaint rate from customers, filter flare-up no longer appears to be a customer problem with cork-on-white tipped products. However, occasional high filter flare-up rates have occurred for cork-on-white tipped products during testing on the smoking machine. The use of modified cork inks containing low levels of silicates, especially at reduced ink weights (3.0 vs. 4.0-4.5 g/m^2), has reduced flare-up during machine testing. Both the Merit-type and the Marlboro-type color standards have been met with the low silicate inks at 3.0 g/m^2 . Subjective and machining acceptability remain to be demonstrated.

b. Tactics and Timetable

(1) Produce Bristol and Merit models in the factory for internal panel testing - April, 1991.

(2) Demonstrate subjective parity of low silicates/low ink weight tippings with current Merit and Bristol tippings - April, 1991.

(3) Conduct round robin ink weight testing with QA Labs to establish a gravimetric ink weight test method for incoming materials inspection - April, 1991.

(4) Conduct initial (one pallet) factory machinability trials of tippings with low silicate inks from Colonial Heights, Hermetite, and Golden Belt - third quarter, 1991.

c. Resource Allocations

Professionals	0.10
Technicians	-
Total	0.10

2. Modify white tipping papers to improve lip release properties by December, 1991.

a. Status

Lip release properties of white tippings are not as good as those of cork tippings. White tippings typically have about 0.5 g/m^2 of nitrocellulose coating to prevent the tipping from sticking to the lips; cork

tippings contain from 1.5 to as much as 5.0 g/m² of cork ink with nitrocellulose included in the formulation. Two approaches are being investigated to improve the lip release characteristics of white tipping: (1) improve the nitrocellulose coating process and (2) improve the basesheet to enhance the barrier properties of the coating. Ecusta used a two-pass coating process to apply 0.9 g/m² of nitrocellulose to the tipping; a slight improvement in lip release rating has been obtained with this tipping. No machinability testing has been conducted to date for the increased coating level. An increased sizing level in Kimberly-Clark's GSR-236M3 tipping has also given a slight improvement in lip release ratings.

b. Tactics and Timetable

(1) Produce factory models of Marlboro Lights 100 with two-pass coated tipping for taste and odor approval - March, 1991.

(2) Determine factory machining performance of Ecusta Marlboro Lights tipping converted with the two-pass coating process - April, 1991.

(3) Evaluate the lip release performance of GSR-236M3 tipping coated with nitrocellulose in a two-pass coating process by Hermetite - April, 1991.

(4) Recommend basesheet and coating combination to give improved lip release properties for white tippings - May, 1991.

c. Resource Allocations

Professionals	0.15
Technicians	-
Total	0.15

D. Resource Allocations for Tipping Paper Project

Professionals	0.25
Technicians	-
Total	0.25

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VII. Wood Pulp Papers

A. Objective - Qualify one or more alternate supplier of wood pulp cigarette paper at each of four porosity grades

B. Strategy - Qualify one or more alternate suppliers of wood pulp cigarette paper at each of four porosity grades.

1. Status

Initial applications of wood pulp cigarette wrappers to generic and price/value brands involve four porosity grades from Kimberly-Clark ranging from 22 to 46 Coresta units in permeability. Ecusta and Wattens wood pulp papers at each of the four porosity grades were evaluated analytically and subjectively. Analytical smoking results showed interchangeability among the three suppliers for each grade. Basic FF KS models made in the factory with 27 Coresta papers from both Ecusta and Wattens were judged to be subjectively acceptable alternatives to the KC control cigarettes by the Richmond Panel. Due to relatively low current usage of wood pulp papers, only the Ecusta material was selected for factory qualification testing. Manufacturing Services is completing the final (truckload) qualification step for Ecusta 27 Coresta paper.

Sample bobbins of wood pulp papers were requested from Papeteries de Mauduit, our third supplier of flax papers, at each of the four porosity ratings. These papers are currently being tested relative to the KC grades for physical properties and analytical smoking performance.

Some difficulties occurred with sideseam adhesion during the initial manufacture of cigarettes at 8000 per minute at Cabarrus using 46 Coresta KC wood pulp paper. Test adhesives from two suppliers were evaluated at Cabarrus with the 46 Coresta paper and gave good seaming performance during a three day trial. Monitoring of seam adhesion quality is continuing.

2. Tactics and Timetable

a. Demonstrate the interchangeability of PDM wood pulp cigarette papers with KC and Ecusta papers to meet analytical smoking requirements (October, 1991).

b. Conduct panel testing to demonstrate subjective acceptability of PDM wood pulp papers (November, 1991).

c. In conjunction with Manufacturing Services, monitor seaming performance with 46 Coresta wood pulp paper (4th Qtr., 1991).

VIII. Products for Aroma Modification of Sidestream

A. Objective - To develop a modified cellulosic incorporating a flavorant or flavorant system covalently bound to the cellulose so that when the modified cellulose is incorporated into cigarette paper, preferably at the wet end of the paper machine, the flavorant will be thermally released when the cigarette is smoked.

B. Introduction and Status

Covalent bonding of a flavorant molecule to either cellulose or starch is a difficult objective since both polysaccharides are insoluble in most solvents. Therefore, reactions must be carried out in a heterogenous system. However, the hydroxyl groups of the polysaccharides provide a point of reaction that can be exploited. The two types of linkages initially under investigation were carbonates and acetals.

Linking a flavorant to a polysaccharide through a carbonate was investigated. Flavor compounds, such as Aromatek 245, can be activated by a 2,3-cyclic carbonate. Ring opening of the cyclic carbonate (**1**) by the hydroxyl groups of cellulose or starch will provide a carbonate linkage between Aromatek 245 and the polysaccharide. Other target molecules are 1,2:3,4-di-O-methylidene α-D-galactopyranose derivatives of α-hexylcinnamaldehyde (**2**) and vanillin (**3**). A chloroformate can be formed at the C-6 position which can then be reacted with starch or cellulose.

Exploration of the linkage of a flavorant to a polysaccharide through a carbonate was conducted using model compounds. Methyl 4,6-*O*-benzylidene-α-D-glucopyranoside 2,3-cyclic carbonate was prepared. Ring opening of the cyclic carobnate group by n-butanol produced methyl 4,6-*O*-benzylidene-2-*O*-butyl-α-D-glucopyranoside and its 3-*O*-iosmer in about equal amount. Pyrolysis of either of the two isomers gave methyl 4,6-*O*-benzylidene-α-D-glucopyranoside, indicating the carbonate linkage is thermally more labile than the acetal linkage of the desired flavor. The direct carbonate linkage of a flavor, rather than the trans-2,3-cylclic carbonate of a glucose derivative of the flavor, remains to be investigated. To this end, a confidentiality agreement was signed between Philip Morris and Aqualon for a joint development project on the preparation of cellulosic bound flavors.

C. Tactics and Timetable

(1) Assemble a technical package for potential syntheses of covalently linked vanillin or ethylvanillin to cellulose or cellulose derivatives (fourth quarter, 1991).

(2) Consult with Aqualon engineers to discuss synthetic strategies (fourth quarter, 1991).

(3) Obtain appropriate bulk supplies of starting materials, such as vanillin chloroformate (first quarter, 1992).

(4) Monitor progress of Aqualon work and obtain analyses of thermal stability and degree of flavor release of modified cellulosics (second quarter, 1992 and continuing).

(5) Investigate handsheet production incorporating modified cellulosics and evaluate flavor release (first quarter, 1993).

D. Resource Allocations

Professionals	1.35
Technicians	0.35
Total	1.70

Resource Allocation Summary

A. Reduced Sidestream

Professionals	11.55
Technicians	4.65
Total	16.20

B. Control of Puff Count and Ash Flaking

Professionals	0.80
Technicians	0.10
Total	0.90

C. Project Tomorrow

Professionals	1.30
Technicians	0.75
Total	2.05

D. Filter Web Development Support

Professionals	0.80
Technicians	0.70
Total	1.50

E. Cigarette Paper Specifications

Professionals	0.65
Technicians	-
Total	0.65

F. Improved Tipping Papers

Professionals	0.25
Technicians	-
Total	0.25

G. Aroma Modification of Sidestream

Professionals	1.35
Technicians	0.35
Total	1.70

Totals For Paper Technology

Professionals	16.70
Technicians	6.55
Total	23.25